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Chemistry-Separation Processes
for Plutonium and Uranium

AN ION-EXCHANGE PROCESS FOR U^{233} ISOLATION AND PURIFICATION

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
CARBIDE AND CARBON CHEMICALS COMPANY
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D. C. Overholt

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OAK RIDGE NATIONAL LABORATORY
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0.0 ABSTRACT

An ion-exchange process for coupling the Interim-23 solvent-extraction separation process for U^{233} to the final metallurgical reduction was developed and satisfactorily demonstrated on a full-scale application. The uranium product was satisfactorily carried through a uranium peroxide precipitation, which is the initial step in the metallurgical reduction process. A mass analysis of the purified product was made.

1.0 INTRODUCTION

The purpose of the ion-exchange process is to concentrate the uranium in the product stream from the Interim-23 solvent-extraction separation, decontaminate it from radioactive and ionic impurities, and convert it to a form suitable for the metallurgical reduction step. A cation-exchange resin was chosen in preference to an anion-exchange resin because present anion-exchange processes involve chloride or sulfate ions, which are more highly corrosive to equipment than the nitrate ion used in the cation exchange. The evaporation process formerly used for concentration of the product was unsatisfactory because no additional decontamination from residual fission products was accomplished and corrosion products present were concentrated. A solvent-extraction process was investigated but was laborious and time consuming. Precipitation of the uranium from dilute solution is undesirable because thorium would be coprecipitated and large-size equipment would be needed.

Studies included chemical development of the process and its application to large-scale, 300 to 400 g, batches. Although laboratory-scale studies were incomplete, the information obtained was sufficient to give a satisfactory process. The product solution was decontaminated considerably from its major impurities, such as protactinium, thorium, corrosion products, and fission products, by the three columns used, namely, a silica gel column, a small Dowex-50 resin column, and a large Dowex-50 resin column. This last column was the main column for absorption of the uranium, and development work was primarily concerned with it.

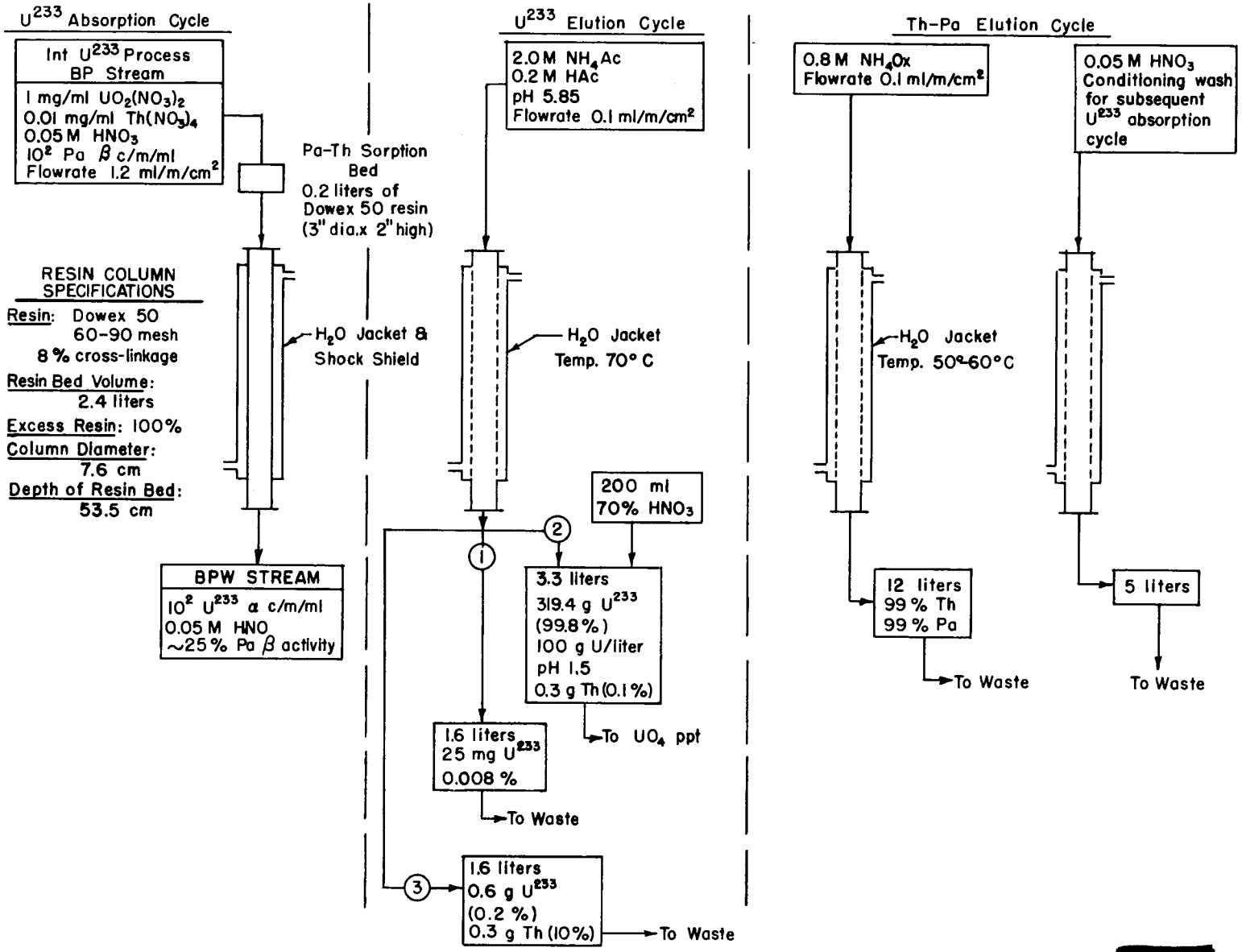
Although the procedure was originally developed for the Interim-23 program, it is applicable to the Thorex process and the 25 process.

2.0 SUMMARY

In this ion-exchange process (Fig. 2.1), which was demonstrated on a 300 to 400-g batch scale, the uranium was concentrated to 75 to 100 g/liter The radioactive impurities remaining in the product, per milligram of uranium, are of the order of 35 β c/min of ruthenium, 20 β c/min of zirconium, 40 β c/min of niobium, 30 β c/min of rare earths, and 0.7 mv of γ activities. The ionic contaminants remaining are 10^{-4} mg of thorium per milligram of uranium and small amounts of such impurities as corrosion products and aluminum. The overall loss of uranium in the process was $\sim 10^{-3}$%.

FIG. 2.1 ION EXCHANGE U^{233} ISOLATION FLOWSHEET

Basis 320 grams



3.0 FEED TO SORPTION COLUMNS

The feed to the sorption columns is the IBP stream from the one-cycle TBP (23) solvent-extraction process. It is 0.05 N in HNO_3 and contains 0.65 g of U^{233}, as uranyl nitrate, per liter. The average volume of feed to the resin column is about 600 liters per run, including cleanout solutions. The principal impurities are thorium, corrosion products, fission products, and aluminum.

4.0 PROTACTINIUM AND THORIUM SORPTION COLUMNS

Before the process stream goes to the main resin column for absorption of the uranium, it passes through a silica gel bed and a small Dowex-50W resin column for removal of the residual protactinium and thorium, respectively. The protactinium is essentially all removed by the silica gel, with negligible loss of uranium. More than 99% of the thorium, which is present in the feed to the extent of about 0.75% of the uranium, is removed by the small Dowex-50W resin column together with some uranium (about 85 g in the four runs), which is eluted and returned to the process stream. These two columns also remove some ionic and radiochemical contaminants.

The silica gel bed, by removing the protactinium from the product stream before it enters the main absorption column reduces considerably the radiation hazard of the large column. The silica gel bed is 36 in. high and 1 in. in diameter and contains 20- to 40-mesh silica gel. One such bed was sufficient to adsorb all the protactinium ($\sim 5\ \mu g$) from four runs. A shorter column possibly could have been used, but previous work had shown that a given amount of adsorbent is more efficient in a long, narrow column than in a short, thick column. Since satisfactory decontamination was obtained with this column and the column was not unwieldy, other sizes were not tried. The uranium loss in the silica gel was about 10^{-3}% (17 mg in the four runs).

The thorium absorption column was 2 in. high and 3 in. in diameter and contained 50- to 100-mesh Dowex-50W resin. Three such columns were used to absorb all the thorium ($\sim$10 g) from the four runs. It was calculated that two columns would be sufficient, but one column leaked and had to be replaced.

The preliminary columns were introduced into the system after it had been observed that thorium and about 75% of the protactinium were absorbed at the top of the uranium-absorption resin column. Since the feed solution in this case had been heated for several hours at 70°C in 0.05 M HNO_3 in an attempt to polymerize the protactinium, it was postulated that the protactinium absorbed was that in the polymerized form.

5.0 URANIUM ABSORPTION

The uranium absorption column is 21 in. high and 3 in. in diameter and contains 50- to 100-mesh, 8% cross-linked, acid-form Dowex-50W resin. The amount of resin used is 100% excess of that theoretically required to absorb the 300 g of uranium in one batch of feed. Absorption is at room temperature and is continuous. The feed flow is downward, and the maximum flow rate is 1 ml/min/cm^2. The uranium loss in the effluent is about 10^{-3}%.

The uranium band on the resin is well-defined, and the amount of uranium absorbed can be determined within ±3% by measuring the height of the band.

Four loadings (three columns, one being reused) were used for the four runs.

5.1 Effect of Varying the Uranium Concentration

The uranium concentration of the feed in the large-scale studies was 0.65 g/liter. In the preliminary studies, in which a 0.75-in.-diameter column was used, concentrations of 0.5 and 1 g/liter were used. There was no significant difference in the uranium loss (10^{-3}%) in the effluent at any of the concentrations studied. The saturation of the resin was 75 to 80% of capacity at all concentrations investigated, and there was no noticeable difference in the spreading of the uranium band on the column.

5.2 Effect of Varying the Feed Flow Rate

A maximum feed flow rate of 1 ml/min/cm^2 was used in the large-scale studies. In the preliminary, small-scale, studies, with a 0.75-in.-diameter column, the flow rates were 8.5 and 15 ml/min/cm^2. There was no difference in the uranium loss in the effluent stream at any of the flow rates investigated. The saturation of the resin with uranium was 70 to 75% of the theoretical capacity at the flow rates investigated.

5.3 Effect of Using Ammonium Form of Resin

There was no significant difference in the uranium loss in the effluent of one run in which the ammonium form of the resin was used. However, the uranium band was considerably easier to observe with the hydrogen-form resin because of the darker color of the ammonium resin.

5.4 Effect of Using 8% and 12% Cross-linked Dowex-50W Resin

Experiments with 8% cross-linked resin showed that this resin absorbs about 10% more uranium than the 12% cross-linked. It is postulated that the 12% cross-linked resin offers a greater steric hindrance to the oxygenated uranyl ion than the 8%.

6.0 URANIUM ELUTION

The uranium is eluted with 2.0 M ammonium acetate in 0.2 M acetic acid (pH 5.85), which flows downward. Flow rates of 0.1 and 0.25 ml/min/cm^2 and temperatures of 50, 70, and 75°C were tried (Figs. 6.1 through 6.4).

The uranium in the eluate is in the form of uranyl acetate, at a concentration of 75 to 100 g of uranium per liter. The product cut contains 99.8% of the uranium on the column. The first volume change, which contains only 0.03% of the uranium, is sent to waste recovery. The 0.2% of the uranium remaining on the column is eluted with the same elutriant in 1.6 liters (tailing cut) and is sent to waste recovery.

6.1 Effect of Varying the Elutriant

Satisfactory elution was obtained with 2.0 M ammonium acetate in 0.2 M acetic acid (pH 5.85) when the column was loaded to 50% of its theoretical capacity. The volume of this elutriant required to elute 99.8% of the uranium (~350 g) was about 4 liters (3.3 column volume changes*). Other elutriants investigated were 6 M HNO_3, 9 M HNO_3, and 0.5 M H_2SO_4, but these all gave excessive tailing.

6.2 Effect of Varying the Temperature and Flow Rate

There was no difference in the elution obtained with flow rates of 0.11, 0.22, and 0.23 ml/min/cm^2 at temperatures of 50, 70, and 75°C, respectively. No attempt has been made at this time to determine the optimum temperature and flow rate.

6.3 Effect of Varying the Column Loading

The columns that were loaded to 50% of their theoretical capacity (Runs 3 and 4) were satisfactorily eluted with the 2 M ammonium acetate—0.2 M acetic acid. Loading of columns to 70% of their capacity (Runs 1 and 2) left less hydrogen-form resin, resulting in higher pH of the flowing stream and precipitation of uranyl acetate in the resin column. Although this would be dissolved subsequently as the concentration of

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* A column volume change is defined as half the volume of the resin bed.

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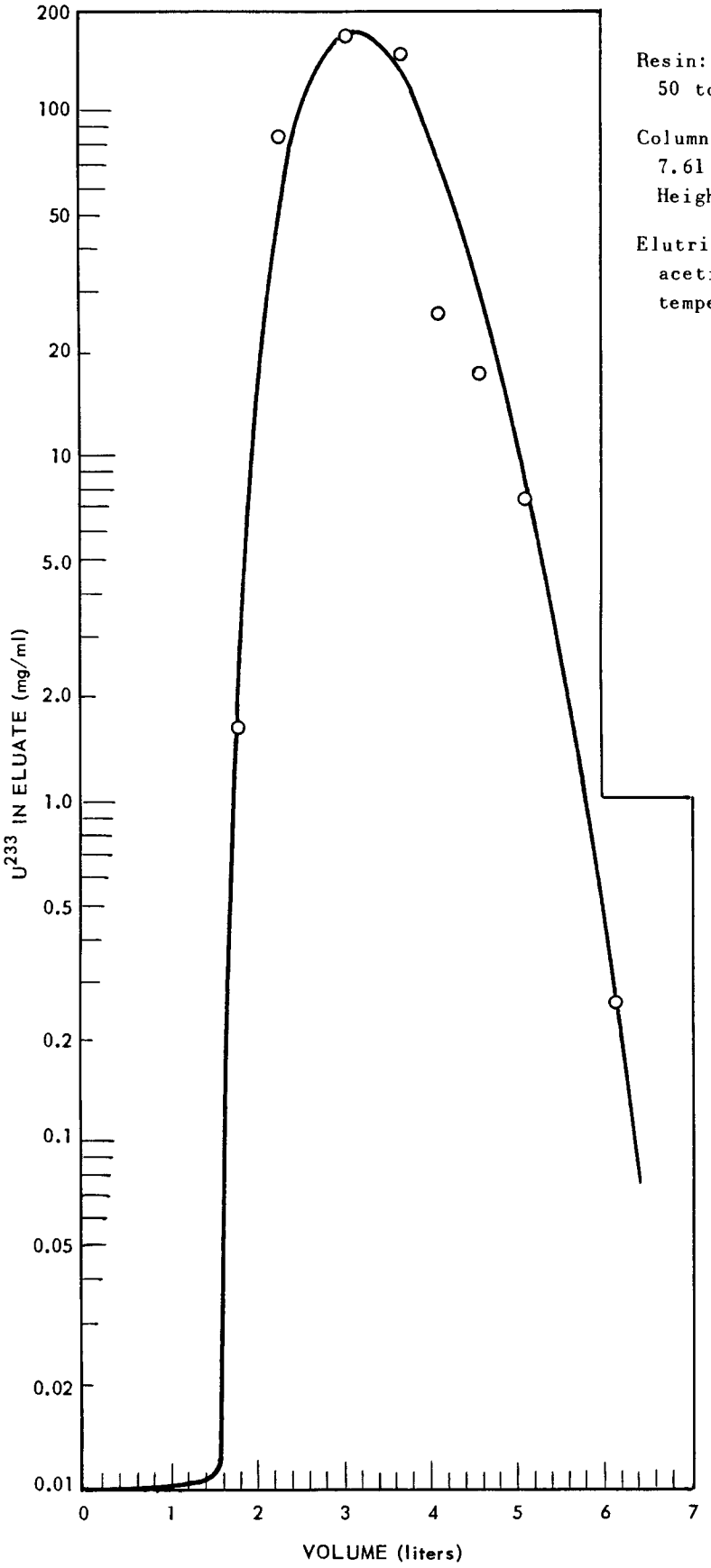
DWG. 15846

Fig. 6.1. Elution of U^{233}, Run 1



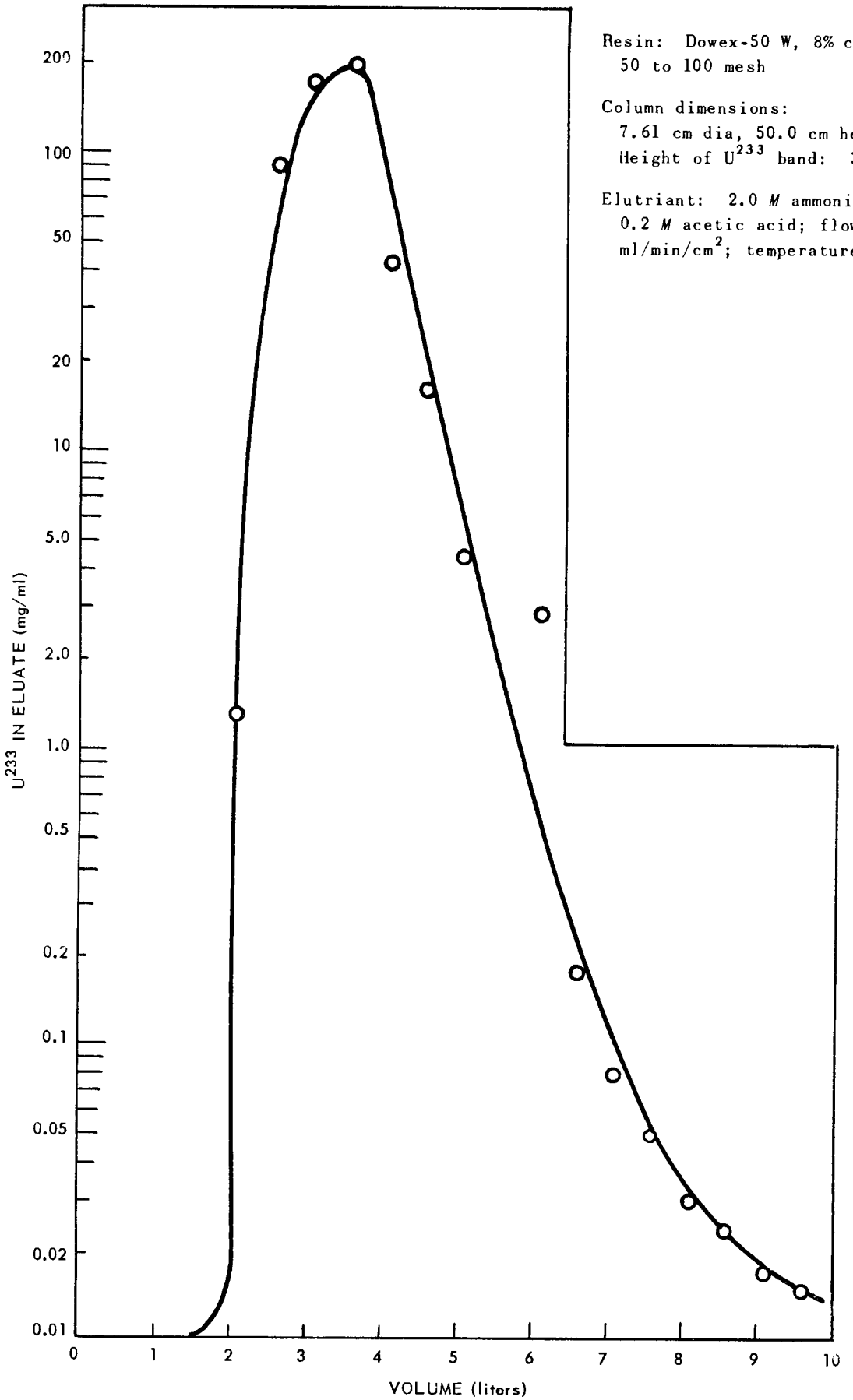
Resin: Dowex-50 W, 8% cross-linked, 50 to 100 mesh

Column dimensions:
7.61 cm dia, 50.0 cm height
Height of U^{233} band: 36.5 cm

Elutriant: 2.0 *M* ammonium acetate, 0.2 *M* acetic acid; flow rate 0.11 ml/min/cm^2; temperature 55°C

Fig. 6.2. Elution of U^{233}, Run 2

[redacted] DWG. 15847



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DWG. 15848

Fig. 6.3. Elution of U^{233}, Run 3

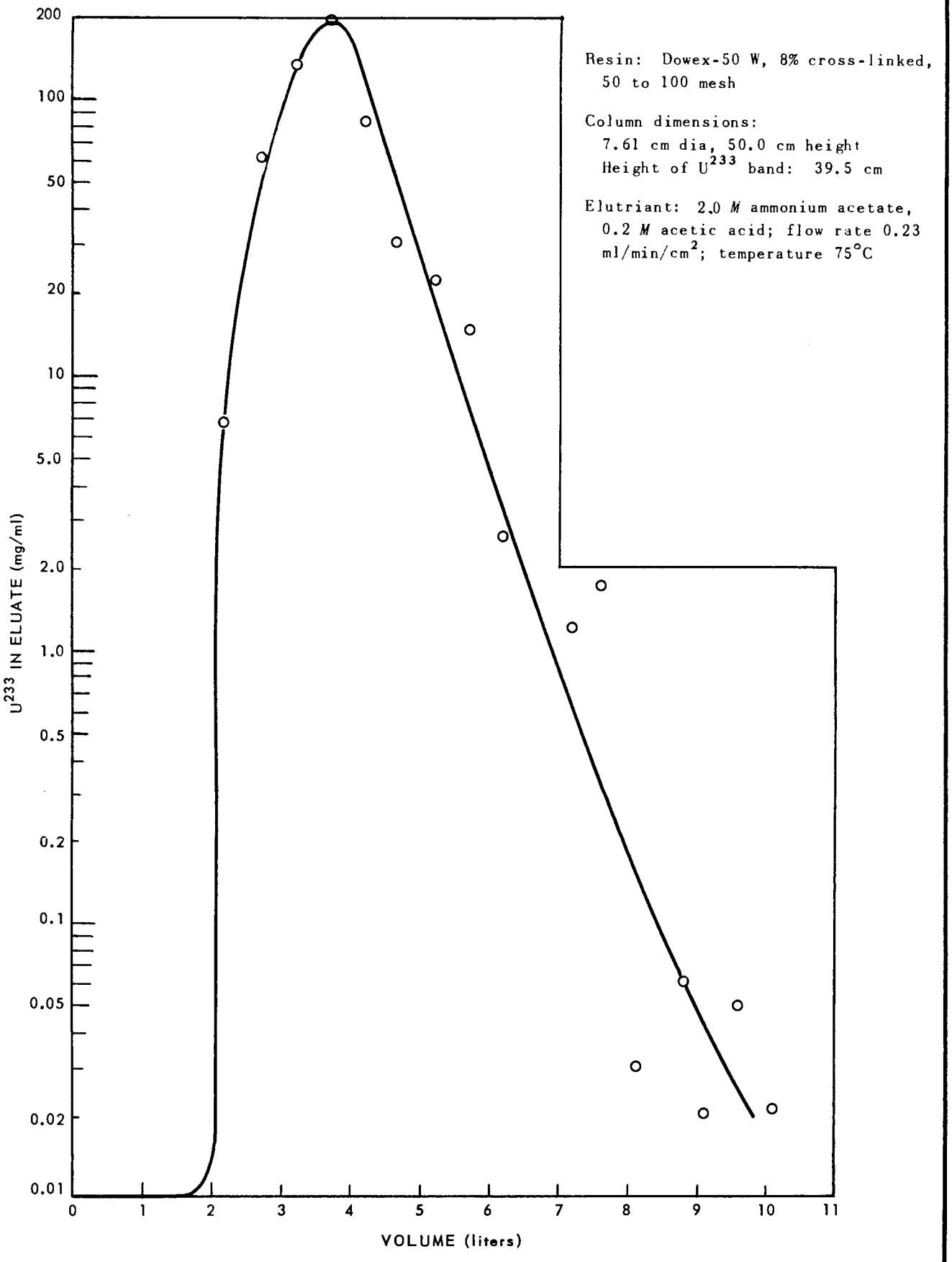
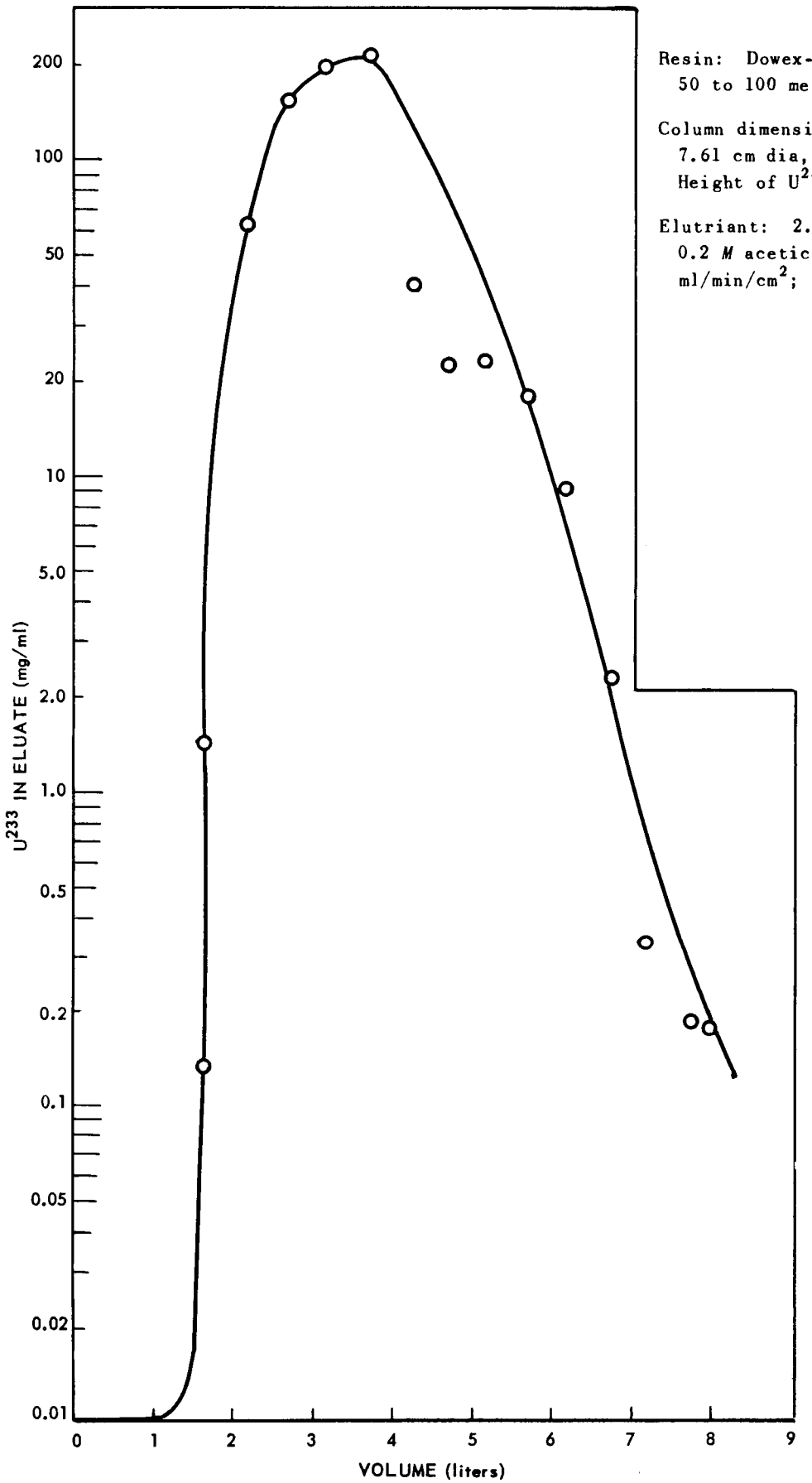


Fig. 6.4. Elution of U^{233}, Run 4

DWG. 15849



the uranium decreased in the eluate, such precipitation might lead to tailing. Therefore, when the column is loaded beyond 50% of its theoretical capacity, more acid may be needed in the elutriant. With loadings above 50%, an elutriant that was 0.4 M in acetic acid gave satisfactory elution; however, when the columns were 50% loaded and then eluted with solution of this acidity, the uranium precipitated in the product cut after standing for a few hours.

7.0 COLUMN CLEANUP

To clean up the main resin column for a subsequent uranium absorption, the resin was washed with about five column volumes of hot (70°C) saturated ammonium oxalate, which effectively removed any residual protactinium, thorium, and iron. (Protactinium would be present if there was leakage through the preliminary columns.) In three runs the oxalate was satisfactorily removed with 6 M HNO_3, which also converted the resin to the hydrogen form. The column was swept free of the strong nitric acid with three volumes of 0.05 M HNO_3 to prepare it for reuse. In one run the 6 M HNO_3 wash was omitted, and the oxalate was swept out with three volumes of 0.05 M HNO_3, leaving the resin essentially all in the ammonium form. The column was reused in this form satisfactorily, but the uranium band was less distinguishable than it was on the hydrogen form resin because of the darker color of the ammonium form resin.

8.0 PRODUCT PURITY

8.1 Radiochemical Decontamination

The activity removed most effectively in the resin isolation process is zirconium, the residual activity of which is 8 to 35 β c/min per milligram of uranium (d.f. ~100). Ruthenium contamination remains in the amount of about 35 β c/min per milligram of uranium (d.f. ~2). Some decontamination from rare earths and niobium is achieved (Table 8.1). The gross gamma activity remaining is around 0.7 mv per milligram of uranium. These values represent the decontamination through the preliminary columns and the main column since the product stream was not sampled after it had passed the silica gel bed or the small resin column.

8.2 Ionic Decontamination

Appreciable ionic decontamination was obtained in the ion-exchange process, with reduction factors ranging from 3 for iron to 378 for magnesium in different runs. The thorium is reduced by a factor of about 10, leaving a thorium contamination of 0.01% of the uranium (Table 8.2).

[redacted]

If it is necessary to reduce the thorium contamination of the eluate below 0.01%, this may be done by precipitating the thorium as the oxalate. In a series of experiments the uranyl acetate solution was made 0.5 M in HNO_3, and a twofold excess of oxalic acid (based on thorium) was added. A thorium reduction factor of 250 was obtained with no detectable loss of uranium.

In an experiment carried out to determine how much thorium could be removed from the product stream by the uranium absorption column alone, a thorium reduction factor of 10 was obtained in the product cut that contained 99.8% of the uranium. In this experiment the thorium contamination of the test solution was about 5% of the uranium. The uranium was eluted with 2 M ammonium acetate—0.2 M acetic acid.

Each column had a 1- to 3-inch band of iron at the top. During the elution, part of the iron band followed the uranium band, while the other part did not appear to move. Since corrosion iron is a mixture of ferric and ferrous forms, it is postulated that the band that followed the uranium was ferric iron, which is known to complex quite strongly with acetate, while the ferrous band remained essentially unmoved. The use of a reducing agent in the feed to the resin column might increase the decontamination from iron.

Table 8.1

Radiochemical Decontamination of Uranium through Silica Gel and Resin Columns

Contaminant	Decontamination Factor			Activity Remaining in Acetate Solution, per mg of U^{233} (β, c/min; γ, mv)			
	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
Gross β	4.7	10.0	8.8				
Ru β	1.7	2.2	3.3		37.4	28.9	43.5
Zr β	109	93	98.5		35.4	8.54	17.9
Nb β	8.3	8.3	3.8		20.0	21.7	64.1
Total rare earth β	16.5		45		65.3	29.8	8.18
Gross γ*	52.2	56.5	91.5	0.86	0.71	0.716	0.698

* As measured with ionization chamber in Bldg. 3550.

[redacted]

[redacted]

Table 8.2

Ionic Reduction Factors through Silica Gel and Resin Columns

Contaminant	Decontamination Factor				Amount Remaining in Acetate Solution (ppm)			
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
Al	84.5	30.3	109.1	45.4	234	220	89.8	118.7
B					70.6	80.1	63.8	61.3
Ca	177	5.14	3.90	3.26	8150	1495	1975	1230
Cr					239	64.0	39.5	30.7
Cu					69.6	42.7	25.0	98.2
Fe	49.5	2.81	5.20	6.90	272	273	177.8	98.0
Mg	378	5.87	5.96	6.45	331	146.7	141	7.16
Mn					210	52.0	76.3	91.0
Ni					135	193.3	71.0	58.3
Pb					979	226.6	224	184
Ti					35.9	13.35	13.16	10.22
Be					< 0.03	< 0.03	< 0.03	< 0.03
Th					34.8	92.3	237	196

[redacted]

Appendix 1

PEROXIDE PRECIPITATION OF URANIUM

The uranium was concentrated to 350 to 480 g/liter by precipitation as the peroxide and redissolution in nitric acid. The uranium loss in the supernatant from the precipitation was about 1 mg per liter of supernatant. The principal residual radioactivity remaining in the product is zirconium (13 to 55 β c/min per milligram of uranium (Table Al.1). Reduction in ionic contaminants is obtained for all those present except beryllium and thorium, both of which are already very low (Table Al.2).

The uranyl acetate solution from the resin column elution was adjusted to varying pH's with 70% HNO_3, and an equal volume of 30% H_2O_2 was added. The uranium peroxide, UO_4, which precipitated was dissolved with about the theoretical amount of 70% HNO_3 by boiling for half an hour in a reflux vessel. The pH's for precipitation of the UO_4 varied from 1.25 to 3.9. No attempt was made to determine which pH was best for the precipitation.

Table Al.1

Decontamination of Uranium through Silica Gel and Resin Columns and Peroxide Precipitation

Contaminant	Decontamination Factor				Residual Activity in Nitrate Solution, per mg of U^{233} (β,c/min;γ,mv)			
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
Gross β	12.81	5.54	10.77	10.0				
Ru β	17.5	17.2	29.3	26.4	8.37	3.66	2.20	2.68
Zr β	93	192	38.8	45.2	54.2	19.95	20.3	13.7
Nb β	40	27.2	62.0	25.3	11.01	6.1	3.03	9.62
Total rare earth β	---	---	1.26	2.47	---	---	18.2	14.93
Gross γ*	37.4	77.6	69.2	110.5	0.676	0.534	0.586	0.582

* As measured with ionization chamber in Bldg. 3550.

[redacted]

Table A1.2

Ionic Reduction Factors through Silica Gel and Resin Columns and Peroxide Precipitation

Contaminant	Decontamination Factor				Amount Remaining in Nitrate Solution (ppm)			
	Run 1	Run 2	Run 3	Run 4	Run 1	Run 2	Run 3	Run 4
Al	84.5	133	165	120	20.9	12.43	12.55	11.2
B					17.0	---	16.5	13.45
Ca	177	3.1	---	7.6	270.1	61.0	---	33.7
Cr					15.07	8.05	6.28	4.92
Cu					4.19	16.8	16.72	2.08
Fe	49.5	12.9	18.1	252	31.0	14.89	10.9	6.73
Mg	378	12.3	---	21.4	15.35	17.55	---	5.37
Mn					16.2	---	1.04	4.93
Ni					29.0	9.03	---	13.45
Pb					97.7	---	---	40.4
Ti					9.77	---	4.18	3.36
Be					<0.03	<0.03	<0.03	<0.03
Th*					34.8	92.3	237	196

* No appreciable thorium decontamination is obtained in the peroxide precipitation process.

[redacted]

Appendix 2

MASS ANALYSIS OF URANIUM PRODUCT

About 98% of the uranium product was found to be U^{233} (Table A2.1). All mass analyses were made on a mass spectrometer with the exception of U^{232}. The U^{232} was determined from its relative α activity as measured on an α-energy analyzer.

Table A2.1

Mass Analysis of Uranium Product

Isotope	Amount (wt. %)			
	Run 1	Run 2	Run 3	Run 4
U^{233}	97.65	98.48	98.58	98.22
U^{234}	0.86	0.52	0.47	0.54
U^{238}	1.49	0.96	0.92	1.06
U^{232}	2.8×10^{-4}	3.7×10^{-4}	2.2×10^{-4}	2.8×10^{-4}
U^{235}	---	0.04	0.03	0.1

Appendix 3

SUMMARY OF DATA ON URANIUM PRODUCT, RUNS 1 THROUGH 4

Table A3.1

Uranium Product Data Summary

Run No.	Product Solution			U (mg/ml)				
	H^+ (N)	Sp. Gr.	Vol. (ml)	By Counting	By Colorimetry	By Macro Titration	By Micro Titration	Total U (g)
1A	3.35	1.6137	438.09	353.64	---	358.95	355.47	157.25
1B	2.30	1.6411	385.78	399.09	---	414.03	416.01	160.424
2	0.1	1.5431	785.84	398.19	402.0	410.35	---	322.47
3	0.50	1.6845	631.34	478.18	485.0	478.59	---	302.15
4	0.40	1.6141	896.81	430.91	460.0	446.94	---	400.82